

AN INVESTIGATION OF THE EFFECT OF COAL PRETREATMENT ON LIQUEFACTION BEHAVIOR

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The effect of coal pretreatment on thermal and catalytic liquefaction behavior was examined in this study. Black Thunder coal, a subbituminous coal from Wyoming, was used untreated and after pretreatment with SO₂. SO₂ pretreatment involved crushing and sizing the coal and then contacting the coarse fraction with aqueous SO₂ to remove alkali and alkaline metals. This treatment was followed by a gravity separation to recover the fraction with the lowest ash content.¹ Analysis of these coals presented in Table 1 indicates that the SO₂ treatment of Black Thunder coal doubles the amount of sulfur in the coal but halves the amount of ash present.

In this study, the effect of different slurry-phase catalyst precursors, most of which were oil-soluble, on the liquefaction behavior of both the untreated and SO₂ pretreated coal was examined. The first set of experiments was performed without a solvent but with the addition of a probe hydrogenation species, pyrene. The second set of experiments was performed with selected catalysts and pyrene but with using a solvent in the liquefaction reactions. The solvents chosen were a non-donor solvent, 1-methylnaphthalene, a coal-derived solvent, V1074, and a hydrogen donor solvent, 9,10-dihydroanthracene. The last set of experiments evaluated the combination of two types of coal pretreatment, in which the untreated and SO₂ treated Black Thunder coals were preswelled prior to liquefaction reactions. The swelling solvents chosen were methanol, isopropanol, tetrahydrofuran and dimethylsulfoxide on the basis of the research performed at Amoco in conjunction with this work.² The liquefaction reactions were performed thermally and catalytically. Ni octoate was chosen as the catalyst because of its demonstrated activity while 1-methylnaphthalene was chosen as the reaction solvent because of its apparent noninteraction with the coal and pyrene system which would allow the effect of preswelling as a pretreatment method to be clearly demonstrated.

EXPERIMENTAL

Catalyst Screening Test. The catalytic activity of a number of different catalysts for coal conversion of untreated and SO₂ treated Black Thunder coal and pyrene hydrogenation was evaluated with and without solvent. The system without solvent was composed of 1.5 g pyrene, 20 wt% coal and a nominal 600-700 ppm of active metal from the catalyst precursor based on the coal feed. The coals used were untreated Black Thunder coal and SO₂ treated Black Thunder coal which were obtained from Amoco. Proximate and ultimate analyses for both coals are given in Table 1. The catalyst precursors tested were molybdenum naphthenate (Shepherd Chemical), iron naphthenate (Aldrich), nickel naphthenate (Shepherd Chemical), nickel octoate (Shepherd Chemical), chromium 2-ethylhexanoate (Strem Chemical), and vanadium naphthenate (Strem Chemical). The reactions were performed using ~20 ml stainless steel tubular reactors at 410° for 30 min and were agitated horizontally at 450 cpm. The pyrene reaction products were analyzed by gas chromatography using a Varian Model 3400, a J&W DB column and flame ionization detection. Pyrene conversion and hydrogenation were used to compare the effect of the catalyst and coal pretreatment on the hydrogenation reactions. Pyrene hydrogenation is defined as the moles of hydrogen required to form the liquid hydrogenation products from pyrene as a percentage of the moles of hydrogen required

to form the most hydrogenated product, perhydropyrene. Coal conversion to THF solubles was also determined.

The reaction systems with solvent employed these different solvents: 9,10-dihydroanthracene, 1-methylnaphthalene, and V1074, a coal derived solvent from the Wilsonville Coal Liquefaction Research and Development facility. The coals used were untreated and SO₂ treated Black Thunder coals. The catalysts employed with the different solvents were nickel octoate, cobalt naphthenate and chromium naphthenate with 9,10-dihydroanthracene; nickel octoate with V1074; and nickel octoate and chromium naphthenate with 1-methylnaphthalene. The reaction conditions used were 410 °, 1250 psig H₂ at ambient temperature, 30 min reaction time, 1.33 g maf coal, 0.67 g pyrene, 2.00 g of solvent, and catalyst loading of 600 to 700 ppm of active metal based on coal feed. The reactors were the same as previously described. The pyrene reaction products and coal conversion were obtained as stated earlier.

Coal Swelling Reactivity Test. For the coal swelling reactivity test, four swelling solvents were used: methanol, isopropanol, tetrahydrofuran, and dimethylsulfoxide, all of which were obtained from Fisher Scientific and were used as received. Untreated and SO₂ treated Black Thunder coals were swelled prior to reaction by introducing 2 g of coal to a swelling tube along with 7 ml of swelling solvent. After 2 hr the amount of coal swelling that occurred was determined by measuring the height of the coal and comparing that to the height of the coal prior to swelling. The coal remained in the swelling solvent for a total of 24 hr, after which the solvent was removed from the coal and dried for 7 hr at room temperature; the weighed coal was placed in the liquefaction reactor and then reacted at 410° for 30 min under well-agitated conditions. Each reaction contained a nominal 1.33 g of maf coal, 2.00 g of 1-methylnaphthalene as solvent, 0.67 g of pyrene, and any residual swelling solvent remaining in the coal for those reactions performed with prior solvent swelling. Hydrogen gas was introduced at 1250 psig at ambient temperature. Reactions were performed thermally and catalytically; the catalyst used was nickel octoate introduced at a level of 600 to 800 ppm of active metal

DISCUSSION OF RESULTS

Effect of Catalyst Precursors on Coal and Pyrene Conversion. Liquefaction reactions were performed with untreated and SO₂ treated Black Thunder coals without a solvent using pyrene as a probe hydrogenation species. The amount of coal conversion, pyrene conversion and pyrene hydrogenation (HYD) achieved with the different catalyst precursors is presented in Table 2. With each catalyst precursor when no solvent was present, the coal conversion was higher with the SO₂ treated coal than with the untreated. In the reactions with Mo naphthenate, the amount of coal conversion was almost doubled, while Fe naphthenate, Ni naphthenate, and Ni octoate showed substantial improvements with the SO₂ treated coal. The catalyst precursors that had the least effect on coal conversion for untreated Black Thunder coal were Mo naphthenate and Cr 2-ethylhexanoate which yielded average coal conversions of 48.1 and 48.0%, respectively.

Pyrene conversion varied considerably depending upon the type of catalyst precursor present and the amount of sulfur present in the system (Table 2). Pyrene conversion for the untreated coal system was greatest with Ni octoate and Ni naphthenate while Mo naphthenate, Fe naphthenate, Cr 2-ethylhexanoate and V naphthenate showed low activity. The presence of the additional sulfur in the SO₂ treated coal affected some of the activity for pyrene conversion for the different catalysts. Mo naphthenate increased substantially from 3.4% in the untreated system to 26.3% in the SO₂ treated system. Cr 2-ethylhexanoate doubled in pyrene conversion but still showed low activity. Ni octoate was active with the SO₂ treated coal just as it was with the untreated coal. The primary hydrogenation product from pyrene observed with all of the catalyst precursors was dihydropyrene

(DHP) while the more active catalysts also yielded tetrahydropyrene (THP) and hexahydropyrene (HHP) as the reaction products.

When solvents were used in the liquefaction reaction in the presence of catalyst precursors, interactions between the solvent and catalyst precursor became apparent. For example, Ni octoate was used with all three solvent systems; for both untreated and SO₂ treated Black Thunder coal, the hydrogen donor solvent, 9,10-dihydroanthracene (DHA), produced the highest coal conversion, followed by coal-derived V1074 with the nondonor, 1-methylnaphthalene (1-MN), yielding the least conversion. The reactions with Cr naphthenate in DHA yielded coal conversions of ~77 and ~79% for untreated and SO₂ treated coals while in 1-MN the conversions with Cr naphthenate were ~53 and ~52%, respectively. Pyrene conversions tended to vary rather substantially and appeared to be influenced by the specific interactions of the solvent with the catalyst and probe pyrene molecule. The highest conversions of pyrene were observed with Ni octoate in 1-MN, but nearly twice as much pyrene conversion was obtained with SO₂ treated coal than with untreated coal. The primary hydrogenation products from pyrene in the reactions with the solvents were DHP; only minor amounts of THP were formed when DHA was solvent while neither THP nor HHP was formed with the other two solvents.

Effect of Solvent Preswelling on Liquefaction Reactions. Four swelling solvents, THF, methanol, isopropanol, and DMSO, were employed to preswell untreated and SO₂ treated coals. The swelling of the SO₂ treated and untreated Black Thunder coals ranked as methanol = isopropanol < THF < DMSO. DMSO swelled the untreated coal by 100% so that the volume of the coal doubled. The other swelling solvents, methanol, isopropanol and THF, swelled the untreated coal by 16 to 42% with THF being the most effective among the three. Methanol and isopropanol remained in the coal in similar amounts which ranged from 0.9 to 1.3 g for 1.6 to 1.7 g of coal. THF showed more inclusion in the coal leaving between 1.45 to 1.7 g in 1.6 to 1.7 g of coal while DMSO left between 3.1 to 4.3 g in 1.62 g of untreated coal.

All of the swelling solvents increased the volume of the SO₂ treated coal more than they did for the untreated coal, although the swelling ranking was the same. Again DMSO remained strongly absorbed in the coal after removal of the swelling solvent with amounts ranging from 4.0 to 5.7 g. By contrast, nearly 2.0 g of THF and about 1.0 g of either methanol or isopropanol was retained in an equivalent amount of coal.

Liquefaction reactions were performed thermally without a catalyst and with Ni octoate. Ni octoate was chosen as the catalyst because of its demonstrated high activity for coal conversion. Table 3 presents the change in coal volume upon swelling, coal conversion and pyrene conversion for both untreated and SO₂ treated coals. The addition of Ni octoate increased the amount of coal conversion achieved regardless of swelling solvent or no swelling solvent. Likewise, pyrene conversion was increased with Ni octoate present in the reaction medium.

The preswelling solvent which showed the most improvement for coal conversion compared to no preswelling for thermal reactions of untreated coal was isopropanol and THF for the SO₂ treated coal. Methanol yielded the greatest improvement in the reactions with Ni octoate for both untreated and SO₂ treated coals. By contrast, DMSO, which was the most effective swelling solvent and had the highest incorporation into the coal, was most detrimental for coal conversion. The SO₂ pretreated coal reacted with Ni octoate was more adversely affected by DMSO than the untreated coal.

Pyrene conversion varied according to the reaction condition. For untreated Black Thunder coal systems, the highest pyrene conversion was achieved with Ni octoate with methanol and without preswelling solvent. For the SO₂ treated Black Thunder coal systems, the highest pyrene conversion was obtained with Ni octoate and no preswelling solvent followed by Ni octoate with DMSO as preswelling solvent. Product distributions achieved from pyrene with coal preswelling yielded DHP

as the primary product for reactions with Ni octoate and occasionally with the thermal reactions depending upon the type preswelling solvent. Some HHP was formed with the Ni octoate systems depending again upon the preswelling solvent.

SUMMARY

SO₂ pretreatment of Black Thunder coal enhanced the liquefaction behavior of the coal in the presence of different catalytic agents regardless of whether a solvent was present or not. A hydrogen donor solvent, 9,10-dihydroanthracene, promoted increased coal conversion compared to nondonor and coal-derived solvents. Pyrene conversion and hydrogenation were highly dependent upon the catalyst type and upon the presence of sulfur in the system. For Mo naphthenate the sulfur in SO₂ treated Black Thunder coal with solvent present promoted pyrene conversion while for Ni octoate, the sulfur was detrimental to pyrene conversion. The presence of solvent in the liquefaction reaction tended to level the amount of pyrene conversion although 1-methylnaphthalene had a lesser effect than did the other two solvents.

Swelling coal prior to liquefaction reactions had a more positive effect with untreated Black Thunder coal than with the SO₂ treated as shown in Table 4. The only swelling solvent that was detrimental to coal conversion for the untreated coal was DMSO while for the SO₂ treated coal only methanol showed an improvement in coal conversion. Hence, coal preswelling was most effective for untreated Black Thunder coal.

NOMENCLATURE

% HYD	=	percent hydrogenation	maf	=	moisture and ash free
1-MN	=	1-methylnaphthalene	PYR	=	pyrene
DHA	=	dihydroanthracene	THF	=	tetrahydrofuran
DHP	=	dihydropyrene	THP	=	tetrahydropyrene
HHP	=	hexahydropyrene			

ACKNOWLEDGEMENTS

We thank the Department of Energy for support of this work under Contract No. DE-AC22-91PC91051. We also sincerely appreciate the strong support of our staff: Janice Johnson, Patricia Sandlin, Frank Bowers, and Joseph Aderholdt.

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Table 1. Proximate and Ultimate Analysis of Untreated and SO₂ Treated Black Thunder Coals^a

Proximate Analysis ^a			Ultimate Analysis ^c		
	Untreated	SO ₂ Treated		Untreated	SO ₂ Treated
% Moisture	11.2	9.9	% Carbon	69.7	70.5
% Ash	5.4	3.1	% Hydrogen	4.9	5.0
% Volatile Carbon	44.5	41.7	% Nitrogen	0.9	0.9
% Fixed Carbon	38.8	45.3	% Sulfur	0.4	0.8
Total	100.0	100.0	% Ash	6.1	3.4
Btu/lb	10606	10993	% Oxygen (by difference)	18.0	19.4

^aCommercial Testing and Engineering Co., Birmingham, AL

^bAs Received

^cDry Basis

Table 2. Effect of Catalyst Type on Coal and Pyrene Conversions Using Untreated and SO₂ Treated Black Thunder Coal With and Without Solvents*

Catalyst	Untreated Black Thunder Coal			SO ₂ Treated Black Thunder Coal		
	% Coal Conversion	% Pyrene Conversion	% Pyrene HYD ^b	% Coal Conversion	% Pyrene Conversion	% Pyrene HYD ^b
No Solvent						
None	59.6±0.9	1.6±0.1	1.0±0.1	57.5±11.5	1.3±0.4	0.8±0.3
Mo Naphthenate	48.1±1.8	3.4±1.7	1.1±0.6	85.7±2.1	26.3±2.5	9.2±0.9
Fe Naphthenate	54.2±11.2	1.4±0.1	1.0±0.3	63.4±2.8	4.9±4.2	2.1±1.6
Ni Naphthenate	62.7±10.9	13.1±6.8	5.7±1.5	73.9±5.7	15.8±0.4	5.7±0.1
Va Naphthenate	64.4	4.2	2.0	66.1±1.8	3.9±0.7	1.9±0.3
Ni Octoate	73.8±6.0	25.6±0.1	9.1±0.0	84.4±7.6	21.9±2.0	7.8±0.7
Cr 2-Ethylhexanoate	48.0±7.9	1.2±0.3	0.8±0.2	54.8±1.5	3.3±1.6	1.5±0.6
Solvent: 1-Methylnaphthalene						
None	49.3±0.8	3.5±1.1	2.1±0.6	47.3±1.1	1.5±1.1	0.7±0.7
Ni Octoate	70.7±4.1	6.8±0.3	2.3±0.1	76.3±4.2	12.5±3.5	4.2±1.2
Cr Naphthenate	52.7±1.8	0.0±0.0	0.0±0.0	51.7±1.1	0.0±0.0	0.0±0.0
Solvent: V1074						
Ni Octoate	81.5±0.9	6.8±4.3	2.4±1.6	82.1±3.0	2.0±2.8	0.7±0.9
Solvent: 9,10-Dihydroanthracene						
Ni Octoate	87.0±1.7	4.4±1.1	2.1±0.3	92.4±5.0	3.7±1.4	1.8±0.5
Co Naphthenate	83.2±0.1	2.1±0.2	1.3±0.1	85.9±0.8	2.7±0.4	1.6±0.3
Cr Naphthenate	76.8±4.2	4.0±0.0	2.6±0.0	78.6±5.7	2.9±1.3	2.0±0.9

*Reaction Conditions: 410°C, 30 min, 1250 psig H₂ at ambient temperature, agitated at 450 rpm.

^bHYD = hydrogenation

Table 3. Effect of Solvent Preswelling on Reactions of Untreated and SO₂ Treated Black Thunder Coal in 1-Methylnaphthalene^a

Catalyst	Swelling Solvent	Untreated Black Thunder Coal			SO ₂ Treated Black Thunder Coal		
		Change in Volume (% ΔV)	Coal Conversion (%)	Pyrene Conversion (%)	Change in Volume (% ΔV)	Coal Conversion (%)	Pyrene Conversion (%)
None	None	NA	49.3±0.8	3.5±1.1	NA	47.3±1.1	1.5±1.1
Ni Octoate	None	NA	70.7±4.1	6.8±0.3	NA	76.3±4.2	12.5±3.5
None	THF	34.2±7.0	59.7±8.9	0.0±0.0	87.6±2.7	58.0±9.5	0.0±0.0
Ni Octoate	THF	41.3±0.6	77.0±0.1	2.4±0.1	97.4±3.7	72.5±5.8	2.2±0.4
None	Methanol	26.7±0.8	53.9±2.8	1.0±0.3	38.4±2.3	41.8±2.4	1.5±0.1
Ni Octoate	Methanol	18.6±0.6	85.5±0.1	10.9±0.4	31.6±7.4	78.6±1.1	4.9±0.8
None	Isopropanol	16.9±5.5	61.7±1.1	0.8±1.1	45.0±0.0	56.4±3.0	1.6±0.1
Ni Octoate	Isopropanol	16.3±3.8	77.6±1.1	2.2±0.4	32.3±6.4	73.9±5.1	3.9±0.6
None	DMSO	111.7±3.7	29.3±4.0	1.2±0.5	176.5±26.2	29.8±3.2	1.3±0.4
Ni Octoate	DMSO	102.4±9.5	63.6±3.6	5.0±0.8	171.6±11.9	50.1±9.5	7.1±1.1

^a Reaction Conditions: 410°, 30 min, 1250 psig at ambient temperature agitated at 450 cpm.

Table 4. Comparison of the Effect of Swelling Solvents on the Liquefaction of Untreated and SO₂ Treated Black Thunder Coal

Swelling Solvents	Untreated Black Thunder Coal Percent Change in				SO ₂ Treated Black Thunder Coal Percent Change in			
	Coal Conversion		Pyrene Conversion		Coal Conversion		Pyrene Conversion	
	Thermal	Ni Octoate	Thermal	Ni Octoate	Thermal	Ni Octoate	Thermal	Ni Octoate
THF	+10.5	+6.3	-3.5	-4.5	37.3	+10.7	-3.8	-10.4
Methanol	+4.6	+14.8	-2.5	4.1	21.3	-5.5	+2.4	-7.6
Isopropanol	+12.5	+6.9	-2.7	-4.6	17.0	+9.1	-2.4	-8.7
DMSO	-20.0	-7.2	-2.4	-1.9	110.0	-17.6	-26.2	-5.5
								ΔV %
								88.1
								35.6
								38.6
								175.0